APPENDIX E

ORGANIC CONTAMINANT MEASUREMENTS IN LOWER DETROIT RIVER SEDIMENTS

ORGANIC CONTAMINANT MEASUREMENTS
IN DETROIT RIVER SEDIMENTS

Progress Report
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Introduction

As part of the In-Place Pollutants Study (IPPS), which is in turn a part of the Upper Great Lakes Connecting Channels Study (UGLCCS), we have performed in-depth trace organic chemical analyses on sediment samples from the Trenton Channel of the Detroit River. The purpose of this research was to identify and quantify both novel and known contaminants of Trenton Channel sediments. The distributions of sedimentary contaminants were used to deduce possible contaminant sources and to model contaminant transport through the Trenton Channel. These data were also compared with chemical and toxicological data generated by other investigators participating in the IPPS.

Study Site

Detroit River and Trenton Channel chemical biological, sedimentological, and hydrological characteristics have been described in detail in our original proposal (Hites and Swackhamer, 1985) and in our initial progress report (Furlong et al., 1987a). A concise summary of these characteristics follows.

The Detroit River, a strait which connects Lake St. Clair to the western basin of Lake Erie, is one of four major channels joining the Great Lakes (Figure 1). The river is 51 km long and drops about 1 m along its length. The flow is primarily southerly, with an average discharge rate of 5200 m^3/sec (Vaughn and Harlow, 1965).

The lower portion of the Detroit River, where the Trenton Channel is located, is a low-energy environment with flows varying from 0.15 to 0.60 m/sec and significant deposition of fine-grained sediment. This portion of the river has an average width of 2000 m and an average depth of 6 to 9 m. Several islands located in this region divide the river into a system of channels, many of which are used as shipping lanes. In order to accommodate large seagoing vessels, some of these channels are dredged; consequently, the

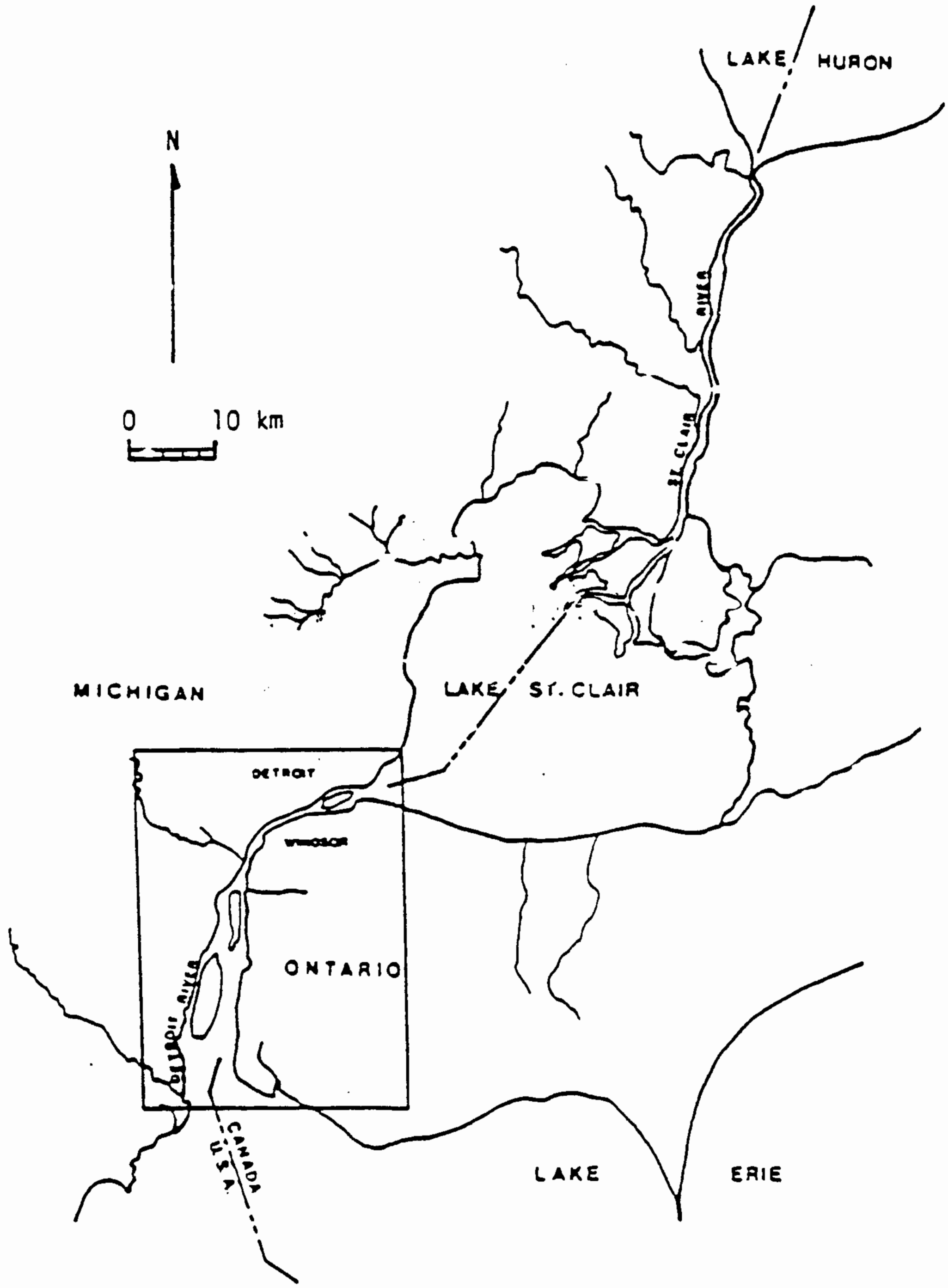

Figure 1 Detroit River study area (from Thornley and Hamdy, 1984).

natural bottom contours of these areas are altered.

The Trenton Channel (Figure 2) is a major channel running between Grosse Ile and the U.S. mainland. The channel is up to 350 m wide and is dredged to maintain a depth of 7 to 9 m, though a small portion along the southern edge of the channel is not dredged and is only 3 m deep (Hites and Swackhamer, 1985). This is one of the sediment depositional zones of the Detroit River. Fine sediments carried from the upper river and from local sources accumulate in this area and in other depositional zones around islands and embayments (Figure 2). Hydrophobic pollutants tend to adsorb onto these fine sediments and can thus become concentrated (Thornley and Hamdy, 1984).

The Detroit River links the upper and lower Great Lakes and is one of the most heavily traveled waterways in the world. In order to accommodate this traffic, heavy dredging is done annually by the U.S. Army Corps of Engineers at the mouth of the Detroit River. A substantial portion of the accumulated material results from industrial and municipal discharge into the river; the discharge level in 1965 was about 3 million kg/day (Vaughn and Harlow, 1965).

Industrial and municipal activities in the area have led to the widespread presence of anthropogenic organic compounds in the water, sediment, and biota of the Detroit River. There are 57 permitted industrial dischargers on the U.S. side and 8 on the Canadian side of the river; collectively these sources discharge over 20 billion L/day into the river (Hamdy and Post, 1985), both upstream of and into the Trenton Channel. The heaviest industrial use of the river is on the U.S. side, from the Rouge River south to the mouth of the Detroit River. Major chemical concerns located along the Trenton Channel are indicated in Figure 2. Many of the industrial wastes are from organic chemical manufacturers and contain significant loadings of complex hydrophobic compounds which subsequently become concentrated in sediments and biota;

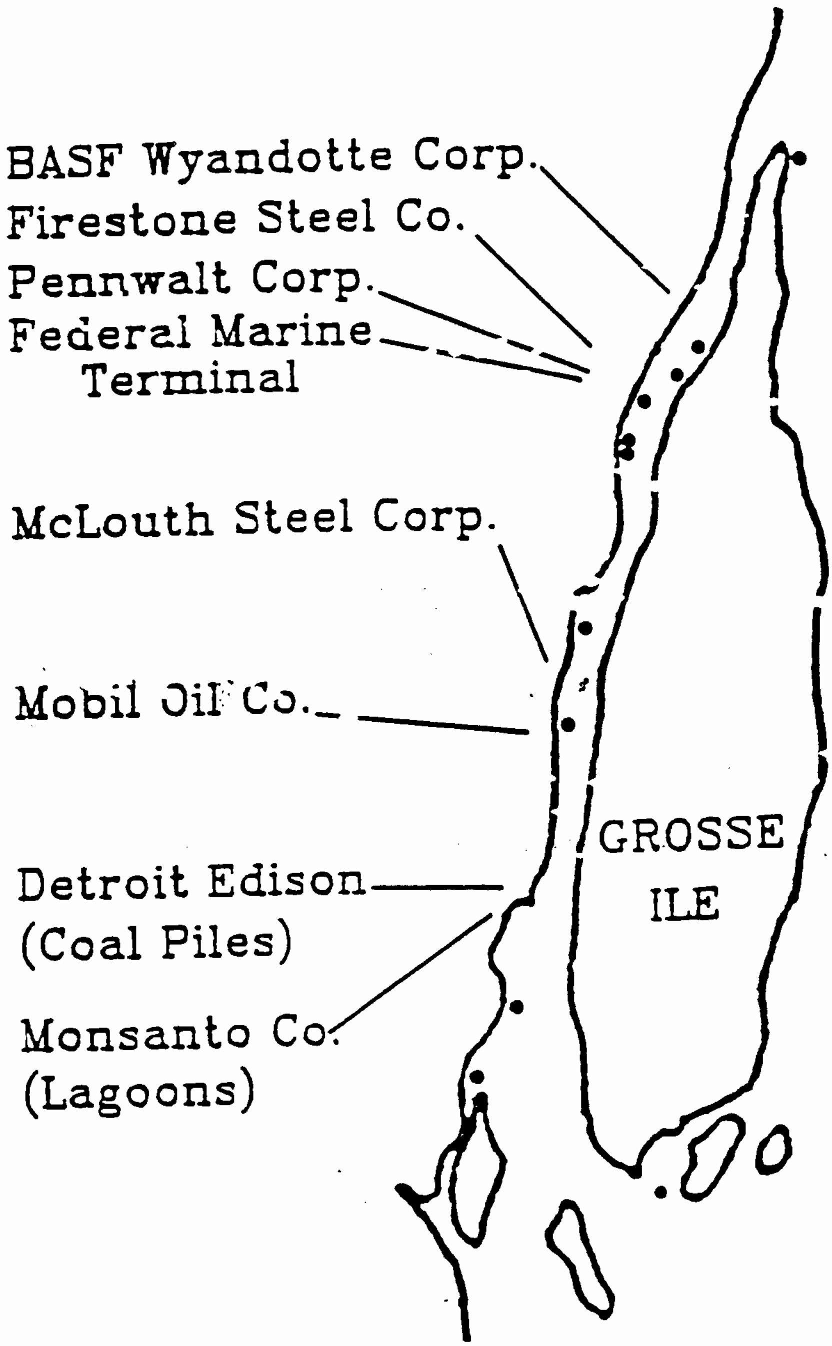

Figure 2. The Trenton Channel of the Detroit River. Sediment collection and major chemical producer locations noted.

consequently it can be expected that previously unidentified, unique organic contaminants might be present in river sediments (Hites and Swackhamer, 1985). In addition to industrial waste, the Detroit River receives the sanitary waste of over 5 million people, including the waste of the largest municipal discharger in the entire Great Lakes Basin, Detroit (population 1.2 million). Municipal outfalls and stormwater overflows have also been identified as contributors to various water quality problems. Over 200 sewage overflows empty into the Detroit River (Everitt et al., 1985). Thus, multiple sources for individual compounds, multiple inputs of complex mixtures, and downstream transport of contaminated sediment make pollutant source identification problematic.

A primary focus of past studies has been the determination of known contaminants present in sediments of the Detroit River. In a 1974 study (Frank et al., 1977), polychlorinated biphenyls (PCBs) and pesticides including DDT, chlordane, dieldrin, and heptachlor epoxide were found in sediments of the river. It was estimated that 3.4 metric tons of PCBs entered Lake Erie each year from sources associated with the Detroit River.

In a reconnaissance study conducted by the Michigan Department of Natural Resources (Fallon and Horvath, 1983), 31 sediment samples were examined for the presence of U.S. Environmental Protection Agency (EPA) priority pollutants. Fifteen different polycyclic aromatic hydrocarbons (PAHs) were found in concentrations ranging from 1 to 40 ug/g wet weight of sediment; several phthalate esters were also found. PCBs were prevalent, with concentrations of 15 to 1700 ng/g. It was noted that a high degree of variability in PCB concentrations exists within depositional zones. Concentrations reported in this study are not directly comparable to the levels found in other studies because the samples used were composites of 50 cm cores rather than surface sediments; such core sampling alters observed concentrations by time averaging.

A reconnaissance study conducted by the Ontario Ministry of the Environment (Thornley and Hamdy, 1984) showed a high degree of PCB contamination (1580 ng/g) in the Trenton Channel, at Fighting Island, and in the Ft. Wayne vicinity. DDT and its metabolites were also found in the Trenton Channel at a level of 186 ng/g. PCB levels were reported to be an order of magnitude higher along the U.S. shore than the Canadian shore.

Several other studies have revealed the presence of organic pollutants in the Detroit River. Hamdy and Post (1985) found PCBs and pesticides, including chlordane, DDT, and hexachlorobenzene, in the mouth of the Rouge River and in the Trenton Channel. Kaiser <u>et al</u>. (1985) detected 24 PAHs and several chlorobenzenes. Platford <u>et al</u>. (1985) measured PCBs, PAHs, and chlorobenzenes, and they noted that PCBs and chlorobenzenes have a very high affinity for sediments, while PAHs partition between the sediments and the water column.

The main objective for this substudy of the IPPS is to identify unknown organic pollutants in Trenton Channel sediments. Due to the large number of organic chemical dischargers, many of these compounds are expected to be structurally unique, and they may also have significant but as yet undetermined toxicological activity. These data can also help interpret the toxicological data which is being generated as part of IPPS. If specific point sources of unusual hydrophobic organic compounds can be determined, movement of sediment-adsorbed compounds can be traced from the Trenton Channel through the lower Great lakes, thus providing geochemical insight into the transport and fate of potentially hazardous organic compounds.

Project Organization and Responsibilities

<u>Project Manager</u>: Ronald A. Hites, Professor, School of Public and Environmental Affairs and Department of Chemistry, Indiana University,

Bloomington, Indiana. Full responsibility for goals outlined in proposal and administration of grant. Responsible for decisions regarding research direction based on first-year results in conjunction with Dr. Mullin, Dr. Kreis, Dr. Giesy, and other principal investigators from the In-Place Pollutants Study.

<u>Project Associate</u>: Edward T. Furlong, Postdoctoral Research Associate, School of Public and Environmental Affairs and Department of Chemistry, Indiana University, Bloomington, Indiana. Responsible for all laboratory analyses and quality assurance. Responsible for protocol development, analysis of samples, data collection, data interpretation. Will work in conjunction with a graduate research assistant, Ms. Donna S. Carter.

Sampling Procedures and Custody

Sediment samples were collected by the U.S. EPA (LLRS), under the direction of Dr. Kreis, in conjunction with Dr. John Giesy, Michigan State University, E. Lansing, Michigan. Samples were collected from approximately 30 sites as designated by Dr. Giesy. Samples remain in the custody of Dr. Giesy except for aliquots shipped to Dr. Hites' laboratory. Formal chain of custody papers were not required for this project.

Analytical Methods

A flow chart of the extraction method is given in Figure 3. Samples to be extracted were homogenized by stirring the entire sample, and an aliquot for percent water determination, about 15-20 g, was removed. Another aliquot (10-30 g) was mixed with 30-70 g clean sodium sulfate to absorb sediment pore water; this resulted in a loose, porous texture suitable for efficient extraction. This mixture was then placed into a glass thimble over a bed of glass wool (to prevent loss of sediment through the bottom of the thimble). The thimble was placed in a Soxhlet extractor and extracted for 24 hours with

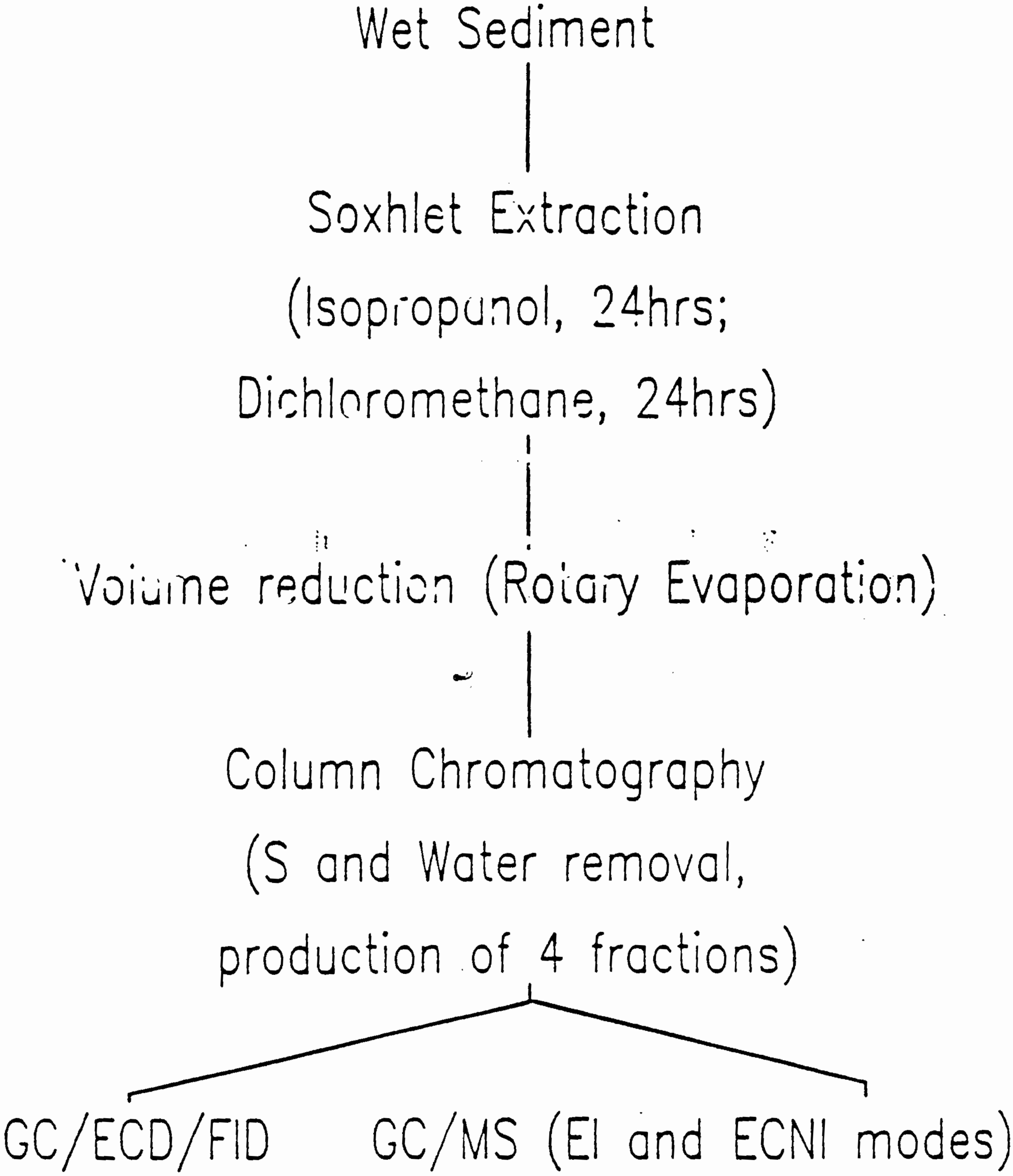

FIGURE 3 SAMPLE EXTRACTION, ISOLATION AND ANALYSIS FLOW DIAGRAM

isopropanol. Just prior to extraction, samples were spiked with 2 internal standards: a PCB (congener 204) and an eight component perdeuterated polycyclic aromatic hydrocarbon (PAH) mixture. The extraction was continued with methylene chloride for a second 24 hours. After extraction, sediments were discarded. The extracts were reduced by rotary evaporation, combined, and solvent-exchanged to hexane.

Combined, hexane-exchanged extracts were column-chromatographed on 20 gram, 1% deactivated silica-gel columns, with HCl-rinsed copper at the bottom to adsorb sulfur and a sodium sulfate "cap" at the top to absorb residual water. The sample was loaded on the column and eluted sequentially with 45 ml of hexane 45 ml of 10% methylene chloride in hexane, 45 ml of 100% methylene chloride, and 45 ml of methanol. All fractions were collected separately. Fraction volumes were reduced, transferred to amber vials, and refrigerated.

The 100% methylene chloride fraction of some sediments (Station 3CC9, for example) was not adequately "cleaned-up" in an 8-inch column of silica-gel, due to the high concentrations of various compounds. These samples required a second clean-up before analysis and were rechromatographed on a second silica column.

Sediment fractions were initially screened, to determine relative compound concentrations, using a Carlo Erba Fractovap 4160 series GC, with dual electron capture and flame ionization detectors installed in series. Sample mixtures were separated on a J&W Scientific fused silica capillary column (30 m x 0.25 mm) coated with a bonded, cross-linked DB-5 liquid phase. Hydrogen was used as the carrier gas, and temperature programming permitted maximum component separation. Dual FID and ECD analog outputs were recorded on a strip chart recorder.

Electron capture, negative ionization GC/MS analyses were performed with a Hewlett-Packard 5985B GC/MS system, equipped with a 30 m x 0.25 mm DB-5 fused silica capillary column. Helium was used as the carrier gas. Methane reagent gas was introduced into the source by a modified transfer line and regulated to an ion source pressure of 0.4 torr. Source temperature was held at 100° C. A GC temperature program, identical to that used for GC screening, was used to maximize compound separation (initial temperature 40° C, held for 4 minutes, temperature increased at 4° C/min to 280°, held for 30 minutes). A range of 50-750 amu was scanned every 1.4 seconds. Emission current was approximately 200 uA, and electron energies were approximately 200 eV.

Polycyclic aromatic hydrocarbons (PAH) were identified and quantified on a Hewlett-Packard 5995 GC/MS system operated in the electron impact mode and equipped with a 25 m x 0.25 mm SE-54 fused silica capillary column (Hewlett-Packard). Helium was used as the carrier gas, and temperature programming (initial temperature 30° C, held for 4 minutes, temperature increased at 10°/min to 160° C, then at 3°/min to 290° C, and held for 34 minutes) was used to achieve maximum PAH component separation. Electron energies were approximately 70 eV.

A selected ion monitoring (SIM) program similar to that used by McVeety (1986) was used for PAH quantitation. Molecular ions of the different PAH were measured in the appropriate GC elution window. Simultaneously, perdeuterated PAH molecular ions were also monitored. Selected ion chromatograms were generated and peak areas electronically integrated. Mixtures of PAH and deuterated PAH (from 50:1 to 1:50) were analyzed in the same manner as samples. From these standard analyses, response factor curves were calculated and used to calculate PAH concentrations for any ratio of PAH to deutero-PAH. Observed ratios of PAH to deutero-PAH varied from approximately 10:1 to 1:3.

Initial quantitation of halogenated aromatics was performed by generating mass chromatograms of selected ions from ECNI-GC/MS total ion chromatograms.

Mass chromatogram peak areas were electronically integrated and compound amounts calculated from response factors for the compound in question relative to PCB congener 204. All halogenated aromatic compound classes were quantified by chlorine homologue (number of chlorines per aromatic base structure). For example, there are 10 possible classes of PCBs quantified in this study, corresponding to the number of possible chlorine substituents on the biphenyl skeleton.

Electron impact GC/MS was also performed on the HP5995 GC/MS using the same column and temperature program as in ECNI-GC/MS analysis. A range of 50-750 amu was monitored. Other instrumental conditions were the same as those used for the PAH SIM-GC/MS analyses.

Extracted sediment dry weights were calculated from percent water determinations. Concentrations are expressed in nanograms compound per gram dry weight of sediment. Procedural blanks were taken through all phases of extraction, isolation, and analysis; final results were corrected for blank contributions, if any.

Quality Assurance

Calibration procedures, analytical procedures, data reduction and validation, internal performance checks, preventive maintenance: We have followed the procedures specified in the original proposal (see CR813524) and standard established procedures from this laboratory. We will also participate in any Quality Control inter-calibration studies which may be requested by the In-Place Pollutants Study Quality Assurance Program.

Specific Procedures Used to Assess Data Precision, Accuracy, & Completeness: All compound identifications were based on an initial match with reference library spectra (when available) and verified by spectra obtained with analytical standards on our instruments. All spectra were visually examined and interpreted--compound identification were not based on library matches only. In our data analysis we also considered laboratory contaminant as indicated by blanks. These were not significant. The types of industry along the Huron-Erie connecting channels were noted in determining the probability of a contaminant source. All data were archived on magnetic tape.

Data Management: All calibration curves, response factors, and compound concentrations were calculated using custom-designed Lotus 1-2-3 spreadsheets. Detroit River sediment individual component and total concentrations for PAHs, PCBs, PCNs, and PCTs were electronically tabulated and stored. Archival back-up copies were also made. Data is available to other investigators in Lotus spreadsheet format, ASCII file format, or as printed tabulations. DIF files can also be generated.

Additional data analysis tools in current or future use include statistical analyses (Microstat, Statpro, and via modem, SAS on an IU VAX cluster), graphics (Sigma Plot, Graph Writer). Three-dimensional data plotting is also being planned. Both parametric tests, such as simple and multiple correlation, and non-parametric tests (including Spearman rank correlations, principal component and cluster analyses) will be used with our completed data set and with data sets exchanged with other PIs.

Quality Assurance/Quality Control: As part of our QA/QC plan, routine procedural blanks were spiked with internal standards and taken through the entire sequence of extraction, isolation and analysis. All results were blank corrected.

In addition, sample replication was assessed by triplicate subsample analyses of samples with high and low contaminant concentrations (Stations 30CR and 25A, respectively) as indicated by initial surveys. Results for PAH are contained in Table 1 and show good replication at both high and low

Table 1. Triplicate PAH results for NBS Standard Reference Material #1649 and High and Low Contaminant Concentration Trenton Channel Sediments.

STA.#, REP.#, RUN #	ng/g DW ACENAPHZ	ng/g DW FLUORENE	ng/g DW PHENAN.	ng/g DW ANTHRAC.	ng/g DW FLUORAN.	ng/g DW PYRENE	ng/g DW B(a)ANTH.	ng/g DW CHRYSENE	ng/g DW B(b)FLU	ng/g DW B(k)FLN	ng/g DW B(e)P	ng/g DW B(a)P	ng/g DW PERY.	ng/g DW B(ghi)PY	ng/g DW COROM	TOTAL PAH (ng/g DW) #
NBS1649 #1	N/A	408	4705	787	7205	5511	3188	429.	12240	0	3485	2855	748	4262	5325	88038
NBS1649 #2	200	386	4804	933	8068	6833	2837	4922	10799	0	3028	2461	0	4117	8270	87023
NBS1649 #3	218	808	4860	896	7729	6245	24 6	.738	11147	0	3280	2414	0	3944	8884	84767
NBS1649 MEAN	209	401	4789	872	7668	6096	2710	4680	11396	0	3246	2577	248	4108	7376	86276
NBS1649 STD. DEV.	9	62	64	62	388	430	342	264	614	0	170	198	351	130	1488	881
NBS1649 STD. DEV.(%)	4	16	1	7	5	7	13	6	5	N/A	5	8	141	3	20	2
STA 25A #1, RUN 1	229	341	1868	713	2301	2183	1088	1602	982	1016	844	1465	414	868	202	15898
STA 25A #1, RUN 2	230	367	1872	709	2413	2204	1069	1846	1066	942	842	1483	411	864	219	15985
STA 25A #2, RUN 1	269	385	1648	816	2087	2067	929	1331	827	813	698	1223	302	720	184	14268
STA 25A #2, RUN 2	278	398	1643	817	2089	2069	939	1373	830	820	711	1238	303	709	189	14421
STA 25A #3, RUN 1	143	249	1258	654	22 1	2247	1419	2053	1390	1238	1084	1896	497	1102	288	17769
STA 25A #3, RUN 2	141	247	1263	667	2265	2228	1402	1999	1343	1300	1108	1948	527	1093	292	17821
STATION 25A, MEAN	215	330	1487	730	2214	2164	1141	1651	1073	1022	876	1542	409	893	229	16019
STATION 25A, S.D.	58	63	16	65	128	75	200	282	224	107	188	287	86	158	45	1411
STATION 25A, S.D.(%)	25	19	11	9	6	3	18	17	21	10	18	19	21	18	20	9
STA 30CR #1, RUN 1	489	924	7809	1918	12447	10078	4871	7743	8836	8487	4430	6813	2022	4701	932	78721
STA 30CR #1, RUN 2	482	904	8344	1374	12427	9964	4600	7852	8784	8202	4849	6636	1941	4871	1087	78104
STA 30CR #2, RUN 1	829	964	6288	4047	17821	1185 2	7207	11457	7431	7398	8782	9107	2694	8998	1373	101607
STA 30CR #2, RUN 2	826	929	6340	4049	17461	11782	7260	11320	7461	7204	8648	9060	2682	8918	1421	100709
STA 30CR #3, RUN 1	312	792	4681	179	12080	9618	4494	7619	8417	8213	4130	6862	1819	4433	1042	69797
STA 30CR #3, RUN 2	319	782	4698	1807	12134	9709	4383	7 89	8794	8480	4221	6421	1836	4409	1118	69916
STATION 30CR, MEAN	864	883	5/32	2591	14062	11177	5411	9880	6270	5998	4748	7390	2132	5002	1164	81476
STATION 30CR, S.D.	64	70	667	1032	2537	1045	1209	1783	884	906	642	1201	329	677	179	13996
STATION 30CR, S.D.(%)	17	8	12	40	18	.7	24	20	14	18	14	16	18	14	15	17

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concentration, and for both individual and total PAH concentrations.

The PAH method was independently checked for precision and accuracy by triplicate analysis of a National Bureau of Standards reference material (SRM 1649; Table 1). Previous application of our analytical technique to this standard (McVeety, 1986; Furlong et al., 1987b; Roll, 1986; Behymer and Hites, 1987) has shown that with our procedure, we consistently reproduce certified PAH concentrations for this reference material.

In addition, we are currently assessing subsample replication of PCBs, PCNs, and PCTs. An EPA Aroclor 1242 (not used for response factor calculations) with a certified congener and homologue composition will be used to assess instrumental precision.

Results

Thirty three sediment samples sent from LLRS were extracted, fractionated, and screened by GC and GC/MS (Table 2). The purpose of this survey was two-fold: first, to determine the presence of commonly quantified compound classes such as PCBs, pesticides, and PAH; and secondly, to identify novel compounds or compound classes that are not commonly quantified. Examination of column chromatographic fractions (see **Methods**) indicated that chlorinated aromatic compounds eluted in the first two of the four fractions and polycyclic aromatic hydrocarbons eluted in the third. However, on a gravimetric basis, better than 50% of the Soxhlet extractable material is contained in the fourth or methanol fraction (see **Methods**). Thus, we have chosen two concurrent approaches to sample examination: First, we quantify the haloaromatics, PAH, pesticides, and any unknowns contained in the first three sample fractions. Secondly, we are using derivatization techniques for the polar compounds contained in the methanol fraction, making them amenable to GC and GC/MS analysis.

TABLE 2. SEDIMENT AND POREWATER SAMPLES RECEIVED AT INDIANA UNIVERSITY FOR DETROIT RIVER PROJECT

SAMPLE #	SEDIMENT EXTRACTED	NCI GC/MS BEGUN	PAH QUANTITATION FINISHED
25	X	X	X
25A	X		X
30	X	X	X
30CR	X	X	X
30UP	X	X	X
30AC	X	X	X
34	X	X	X
41	X	X	X
42	X	X	X
43	X		X
44A	X	X	X
45	X	X	X
47	X	X	X
49	X	X	X
51	X		X
52	X	X	X
53	X	X	X
54	X		X
59A	X		X
77	X	X	X
82	X		X
83	X	X	X
104	X	X	X
105	X	X	X
107	X	X	X
110	X	X	X
111	X	X	X
112	X	X	X
113	X		X
114	X		X
901	X	X	X
902	X	X	X
903	X	X	X

Below we discuss quantitative results for PAH and PCBs, as well as for two relatively unknown compound classes, the polychlorinated naphthalenes (PCNs) and polychlorinated terphenyls (PCTs). These four compound classes, with some minor contributions from pesticides, are the major anthropogenic compounds eluting in the first three chromatographic fractions.

As stated in **Methods**, our initial quantitation of the PCBs, PCNs, and PCTs were based on mass chromatograms generated from ECNI-GC/MS total ion chromatograms. Concentrations varied over three orders of magnitude for each compound class so a quasi-logarithmic classification system has been employed to graphically illustrate compound concentrations. Note that quantitation is based on an internal standard and that total PCBs, PCNs, and PCTs are the sum of the concentrations of the different chlorine homologue class concentrations. Results below are discussed as individual compound classes (including PAH), and an integrated summary follows.

<u>Sedimentary</u> <u>Polycyclic</u> <u>Aromatic</u> <u>Hydrocarbons</u>: Fifteen polycyclic aromatic hydrocarbons (PAH) were quantified in fraction 3 (100% dichloromethane) of the sediment extracts. The separation and quantitation technique has reproduced NBS-certified PAH concentrations in air particulate material (McVeety, 1986; Roll, 1986; Furlong <u>et al</u>. 1987b) and is sensitive to 100 picograms of PAH.

Sedimentary PAH concentrations are listed in Table 3 for the all sediment samples received. Individual PAH concentrations vary from 4 ng/g to 22,000 ng/g dry weight. Individual and summed PAH concentrations were compared for all stations using a correlation matrix. There is an extremely high degree of correlation between all individual PAH and summed PAH (arithmetic mean $r=0.869\pm0.098$, $n=120$). This suggests that the relative amounts of each PAH are similar across a wide range of absolute concentrations. It also suggests either a single PAH source or multiple sources, which are not significantly

Table 8. Sedimentary Polycyclic Aromatic Hydrocarbon Concentrations in the Trenton Channel, Detroit River.

SITE #, REP. #, RUN #	ng/g DW ACENAPHTH	ng/g DW FLUORENE	ng/g DW PHENAN.	ng/g DW ANTHRAC.	ng/g DW FLUORAN.	ng/g DW PYRENE	ng/g DW B(a)ANTH.	ng/g DW CHRYSENE	ng/g DW B(b)FLN	ng/g DW B(k)FLN	ng/g DW B(e)P	ng/g DW B(a)P	ng/g DW PERY.	ng/g DW B(ghi)PY	ng/g DW CORON	TOTAL PAH (ng/g DW)
28A	218	880	1489	730	2284	2164	1141	1651	1073	1022	876	1842	409	898	229	14019
28	526	1431	2808	2234	4489	4416	2068	3708	1866	1880	1604	2033	648	1517	861	31433
30	380	807	3629	1479	8408	4912	3134	8324	2987	2736	2087	8696	914	2029	752	38710
30MC	84	187	812	321	1406	1764	658	1007	941	849	714	1123	317	648	193	10486
30CR	366	883	8452	2590	14062	11877	8414	17980	6220	8996	4748	7390	2132	8002	1186	81476
30UP	271	862	2279	778	3827	3161	2676	1447	1073	1877	1404	2390	756	1621	670	26830
34	160	370	1888	840	3139	2916	1358	2432	2083	1376	1836	2404	740	66	418	21136
41	288	812	2322	1139	4006	3453	1893	2836	2010	1736	1594	2814	778	1632	389	27300
42	339	717	2871	962	4347	4182	2154	3806	3489	1245	2518	3449	1019	2498	636	34190
43	1148	327	1023	349	2801	3102	2814	2282	1997	864	1509	2011	839	1176	440	22876
44A	182	231	1599	688	3931	3270	1617	2871	1868	1946	1406	2810	648	1467	332	24261
45	182	283	1609	486	3283	2914	1413	2680	1961	1018	1708	2463	666	1644	419	28811
47	138	282	1248	697	2717	2626	2082	1967	1308	1110	998	1970	822	969	437	19068
49	126	206	1158	397	2025	1693	912	1397	1086	841	986	161	333	862	182	12330
51	10	22	116	37	214	212	117	112	236	0	81	120	36	72	82	1436
52	0	0	50	9	37	88	17	62	87	0	26	33	4	27	0	362
53	58	165	688	243	1411	1686	1268	1587	2309	0	1137	1828	482	1108	262	17925
54	104	290	1468	619	2689	2492	2247	2103	1741	1709	1381	2889	723	1538	808	22196
59A	60	168	876	349	837	1430	1568	1456	1864	1176	1090	1801	470	1040	228	14809
77	288	882	2297	889	4033	3802	2895	2768	2581	2273	1947	3788	971	1620	687	31243
82	0	8	64	20	119	115	105	78	167	0	74	74	0	84	18	893
83	0	0	100	41	209	163	69	114	101	84	73	108	41	64	0	1172
104	198	377	1804	463	1987	1727	1477	1243	1398	1208	986	1873	446	987	297	18803
106	280	471	2099	649	20446	2879	3510	2404	2122	1393	1810	2128	727	1681	367	40946
107	817	1638	8341	1598	6023	8469	2479	3480	3270	2118	2639	3703	1150	2367	681	43175
110	918	1782	14960	3270	22521	20094	9164	12278	9784	6284	7865	9889	2991	7640	1677	130778
111	474	789	4464	1614	8133	4843	2664	4248	3117	2987	3111	4415	1393	4138	1103	44030
112	819	1190	8270	2010	7112	7060	3611	6931	4678	4217	4232	6112	1651	3931	951	89636
113	46	78	484	139	962	936	46	872	628	608	868	817	212	496	92	7846
114	48	118	879	141	1171	1031	479	909	681	618	626	666	201	489	117	7683
901	481	889	2628	1670	8143	4323	4196	3799	8302	0	2087	3863	1143	1818	778	37890
902	83	180	627	167	1673	1884	1018	1267	2069	0	918	1001	360	809	364	13271
903	0	49	336	47	491	331	177	228	377	0	188	140	0	134	49	2819

different in relative PAH composition or which are well mixed prior to sedimentary PAH deposition.

In addition to being compositionally uniform, the presence of significant quantities of photo-reactive PAH (such as anthracene and benzo(a)anthracene) in Trenton Channel sediments suggests that a PAH source other than combustion derived atmospheric particulates contributes to the observed PAH signal. In sediments and atmospheric particulates collected at remote sites, where PAH adsorbed on particulates would have had significant exposure to sunlight, phenanthrene/anthracene and benzo(e)pyrene/benzo(a)pyrene ratios are 16 and 2, respectively (McVeety, 1986; Furlong et al., 1987b). This reflects the relatively short photolytic half-lives of benzo(a)pyrene and anthracene (Behymer and Hites, 1985). In contrast, Trenton Channel sediment ratios are 2.5 for phenanthrene/anthracene and 0.93 for benzo(e)pyrene/benzo(a)pyrene.

Total PAH concentrations measured in this study compare reasonably well with concentrations calculated from the data of Fallon and Horvath (1983) for 6 stations in the Trenton Channel study area. Due to the dynamic nature of the Trenton Channel sediment environment, large concentration differences are observed over short distances in both data sets (see Figure 4), and results are not directly comparable on a point-to-point basis.

Total PAH concentrations (50-130,000 ng/g DW) are highest at Stations 110, 112, and 30CR (see Table 3 and Figure 4). Stations 30CR and 110 are located in the vicinity of the Pennwalt and Wyandotte Chemical companies and the Federal Marine Terminal, a hazardous waste disposal site. Station 112 is located offshore of Elizabeth Park and a Mobil Oil outfall. These are potentially significant sources of PAH to the immediate vicinity. However, locally high PAH concentrations at sites more distant from PAH point sources are less easily explained. Deposition of PAH rich, fine-grained particles in certain

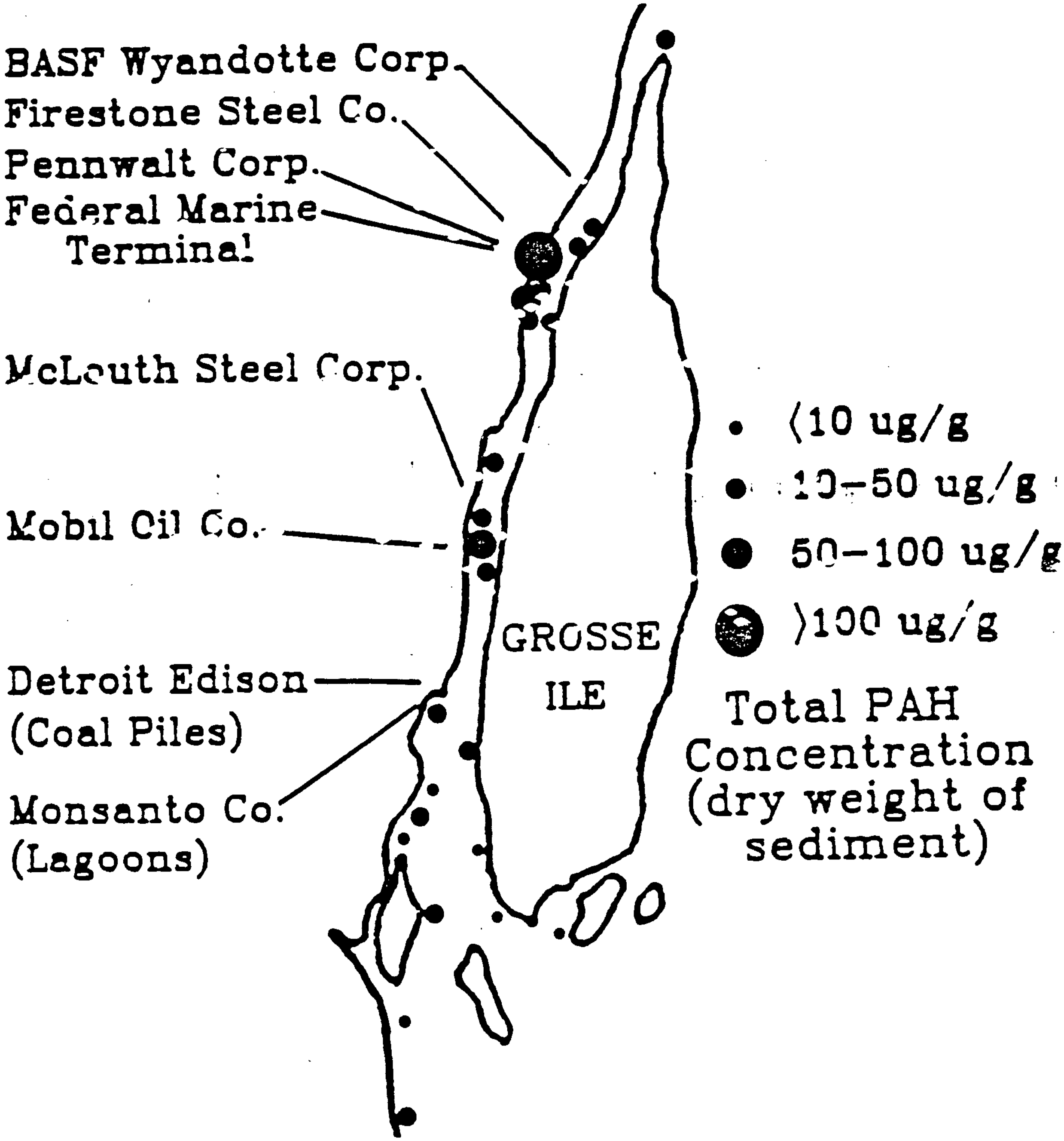


Figure 4 Trenton Channel sedimentary total PAH concentration distributions.

regions (Fallon and Horvath, 1983) is likely to be a major complicating factor.

PAH concentrations throughout the Trenton Channel are, however, indicative of significantly contaminated sediments. Sediment samples from remote sites typically contain PAH concentrations under 10,000 ng/g (Furlong et al. 1987a), in comparison to total PAH concentrations of up to 130,000 ng/g in Trenton Channel sediments. This is particularly remarkable given that the likely residence time of Trenton Channel sediments is short, suggesting that the yearly throughput of PAH is high. The Detroit River-Trenton Channel could be a significant PAH source to Lake Erie, both in the western region and lakewide, depending on the dynamics of lake sediment transport. Jaffe and Hites (1986) inferred rapid (< 1 year) transport of fluorinated aromatic contaminants from the Niagara River to the entire depositional region of Lake Ontario. A similar process could be invoked in Lake Erie for particle-bound PAH.

PCBs: PCBs are a well recognized environmental contaminant; they have been identified in sediments, water, air and biological tissues from both pristine and highly polluted environments (Erickson, 1986; Kimbrough, 1980). Previous investigations of Detroit River sediments have indicated PCB contamination varying from below detection to 3,800 ppb (Hamdy and Post, 1985; Kaiser et al., 1985). Total PCB distributions (sum of Cl_3 to Cl_{10} homologues) are illustrated in Figure 5 for a 12 sample subset of the total sample set. Table 4 contains total PCB and individual chlorine homologue concentrations for these same samples.

Several points can be made regarding PCB distributions. The first is that, within the Trenton Channel, highest PCB concentrations occur at Station 110 and decrease significantly both upstream and downstream from the station. Also total PCB concentrations are elevated in several downstream stations

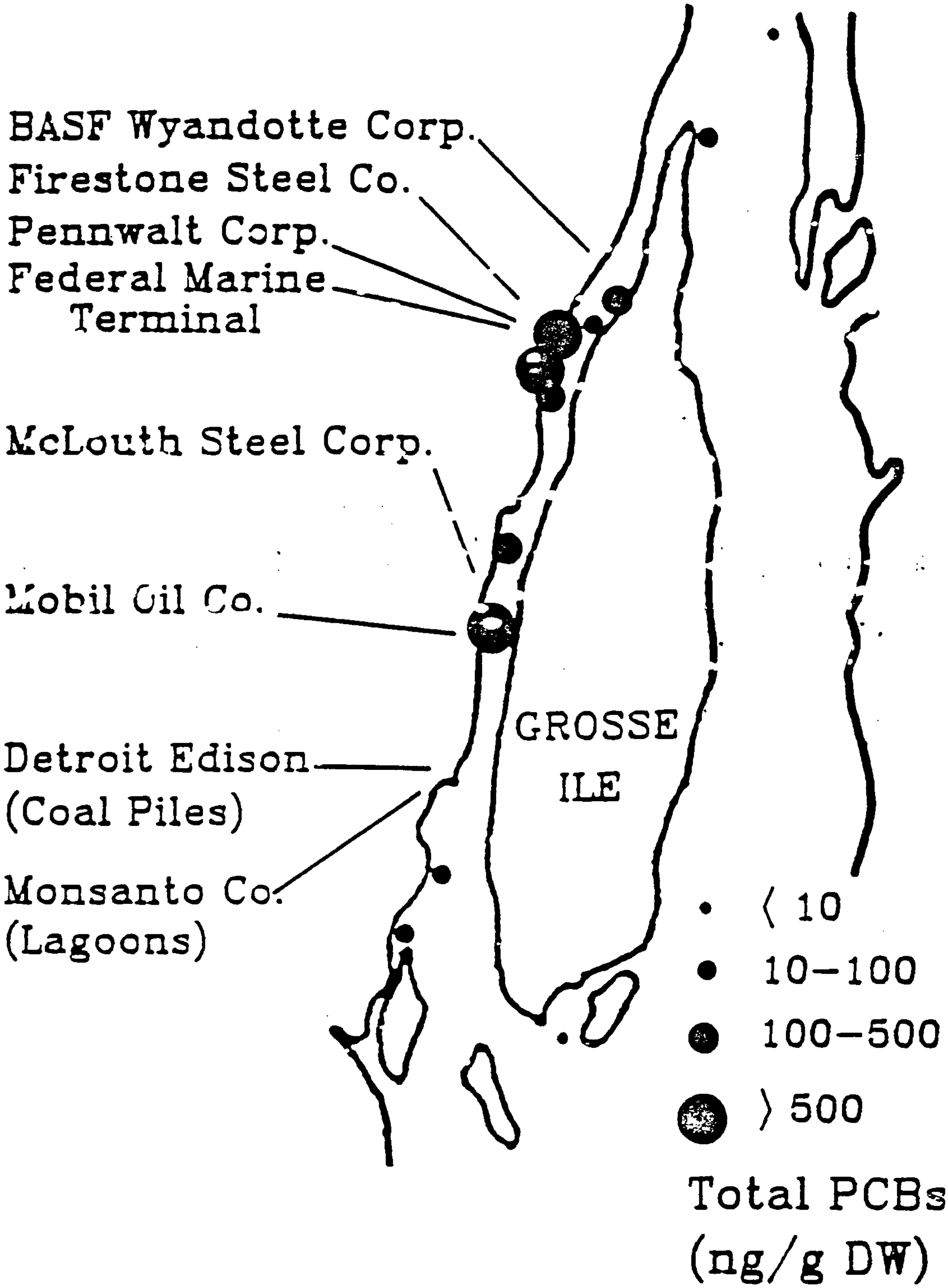


Figure 5 Trenton Channel sedimentary total polychlorinated biphenyl (PCB; sum of chlorine homologue) concentration distributions.

Table 4

Trenton Channel Sedimentary Polychlorinated Naphthalene (PCN), Biphenyl (PCB) Concentrations (ng/g Dry Weight). Concentrations of individual Cl homologues

STATION #	PARENT COMPOUND: Cl-HOMOLOGUE:	PCN Cl-2	PCN Cl-3	PCN Cl-4	PCN Cl-5	PCN Cl-6	PCN Cl-7	PCN Cl-8
25A	25A	n.d.	0.08	0.15	1.5	13	14	0.44
30	30	0.20	60	25	16	170	245	15
30CR	30CR	n.d.	34	20	8.[illegible]	2[illegible]	16	0.60
34	34	n.d.	10	3.8	1.9	9.3	6.9	0.39
52	52	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
77	77	n.d.	4.1	0.50	n.d.	n.d.	n.d.	n.d.
83	83	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
110	110	2.7	450	510	190	480	210	4.0
111	111	n.d.	33	6.1	7.7	[illegible]4	9.9	n.d.
112	112	n.d.	84	46	23	67	54	2.2
113	113	n.d.	9.0	3.5	2.3	5.7	2.6	n.d.
114	114	n.d.	8.1	3.4	0.[illegible]	4.0	2.5	0.06

PCB Cl-4	PCB Cl-5	PCB Cl-6	PCB Cl-7	PCB Cl-8	PCB Cl-9	PCB Cl-10	PCT Cl-11	TOTAL PCNs	TOTAL PCBs	TOTAL PCTs
0.02	1.1	11	18	4.7	0.16	0.02	n.d.	29	35	n.d.
0.03	2.4	37	110	62	3.[illegible]8	2.[illegible]	1900	530	210	1900
0.30	13	170	350	160	4.05	1.1	870	100	700	870
0.27	5.9	60	130	55	1.93	0.72	720	32	260	720
n.d.	0.01	0.18	0.23	n.d.	n.d.	n.d.	n.d.	n.d.	0.42	n.d.
n.d.	0.36	8.8	27	9.1	0.22	n.d.	n.d.	4.6	46	n.d.
n.d.	0.02	0.19	0.13	n.d.	n.d.	n.d.	n.d.	n.d.	0.34	n.d.
0.26	17	110	230	220	25.8[illegible]	25	15000	1[illegible]00	620	15000
0.22	4.1	51	100	31	1.19	n.d.	78	9[illegible]	190	78
1.1	19	170	370	160	5.51	2.3	3600	280	730	3600
0.04	1.3	11	19	3.4	0.09	n.d.	9.8	23	35	9.8
0.07	1.7	19	39	8.1	0.31	0.21	3.7	19	68	3.7

(Figure 5). The observed distribution is similar to total PAH (Figure 4), and can arise from two processes: (1) input from a local source at Station 110, and (2) concentration of fine-grained, contaminant enriched sediments in deposition zones coinciding with locations of high PCB containing samples. Significant sedimentary PCB contamination upstream and downstream of the Trenton Channel has been previously observed (Oliver and Bourbonniere, 1985; Kaiser et al., 1985); this suggests multiple sources of PCBs contributing to sediment transported through the Trenton Channel. Thus, Trenton Channel sediment PCB contamination cannot be unambiguously identified as resulting from within channel contamination or pre-contaminated sediment transport.

Concentrations and distributions of PCB chlorine homologues may provide more geochemical and source information. In the United States, commercial PCB mixtures were distributed primarily as 1200 series Aroclor mixtures by the Monsanto Company, and these mixtures had relatively well defined percentages of Cl-homologues in each mixture (Hutzinger et al., 1974; Brinkman and de Kok, 1980). Many previous PCB analytical methods have attempted to quantify environmental PCB contamination in terms of the concentration of an Aroclor mixture (Erickson, 1986). However, observed PCB distributions can reflect differential degrees of solubility, sediment adsorption, vaporization, and bioaccumulation; this is reflective of a compound class containing the range of solubilities, heats of vaporization, and other chemical properties exhibited by PCB chlorine homologues (Pearson, 1982).

Chlorine homologue compositions observed in Trenton Channel sediments are skewed towards higher chlorine homologues, as would be expected from homologue volatility, adsorption, and solubility (Hutzinger et al., 1974). Significant concentrations of decachlorobiphenyl may result from direct inputs of this homologue which was commercially produced and imported into the United States in significant quantities (Brinkman and de Kok, 1980). However, di- through nona-chloro PCB homologue distributions in Trenton Channel sediments (Table 4), when compared to Aroclor homologue compositions (Hutzinger et al., 1974), suggest possible alteration from original source materials.

Polychlorinated Naphthalenes

Polychlorinated naphthalenes (PCNs), a chlorinated aromatic class analogous to PCBs, have been commercially produced since World War I. They have similar physical and chemical properties as PCBs, but since the introduction of PCBs in 1929, they have been a much smaller fraction of commercial haloaromatic production (about 10% of PCB production; Brinkman and de Kok, 1980). Commercial uses of PCNs prior to the 1950's were as dielectrics, water repellants, and lubricants. After the 1950's production declined and since 1973, the major use has been in automobile capacitors (Brinkman and Reymer, 1975).

Environmental PCN concentrations have not been extensively reported (Kimbrough, 1980). PCNs have been noted in Detroit River samples but not previously reported (M. Mullin, personal communication). Trenton Channel total PCN concentrations for the 12 sample subset are mapped in Figure 6 and total PCN and individual Cl homologue concentrations are listed in Table 4.

Total PCN distributions are similar to total PAH and PCBs (Figures 4 and 5), with highest concentrations at Stations 110, and decreasing concentrations downstream. Since PCN concentrations have not been commonly reported for other Detroit River samples, it is not clear whether PCN contamination is systemic in the Detroit River or localized in the Trenton Channel.

Compositional alteration of sedimentary PCN chlorine homologue distributions is expected to be similar to the previously discussed PCBs. However, compositions of commercial PCN mixes (Halowax 1000 series) are more variable. However, octachloronaphthalene is identified in sedimentary PCNs and was not

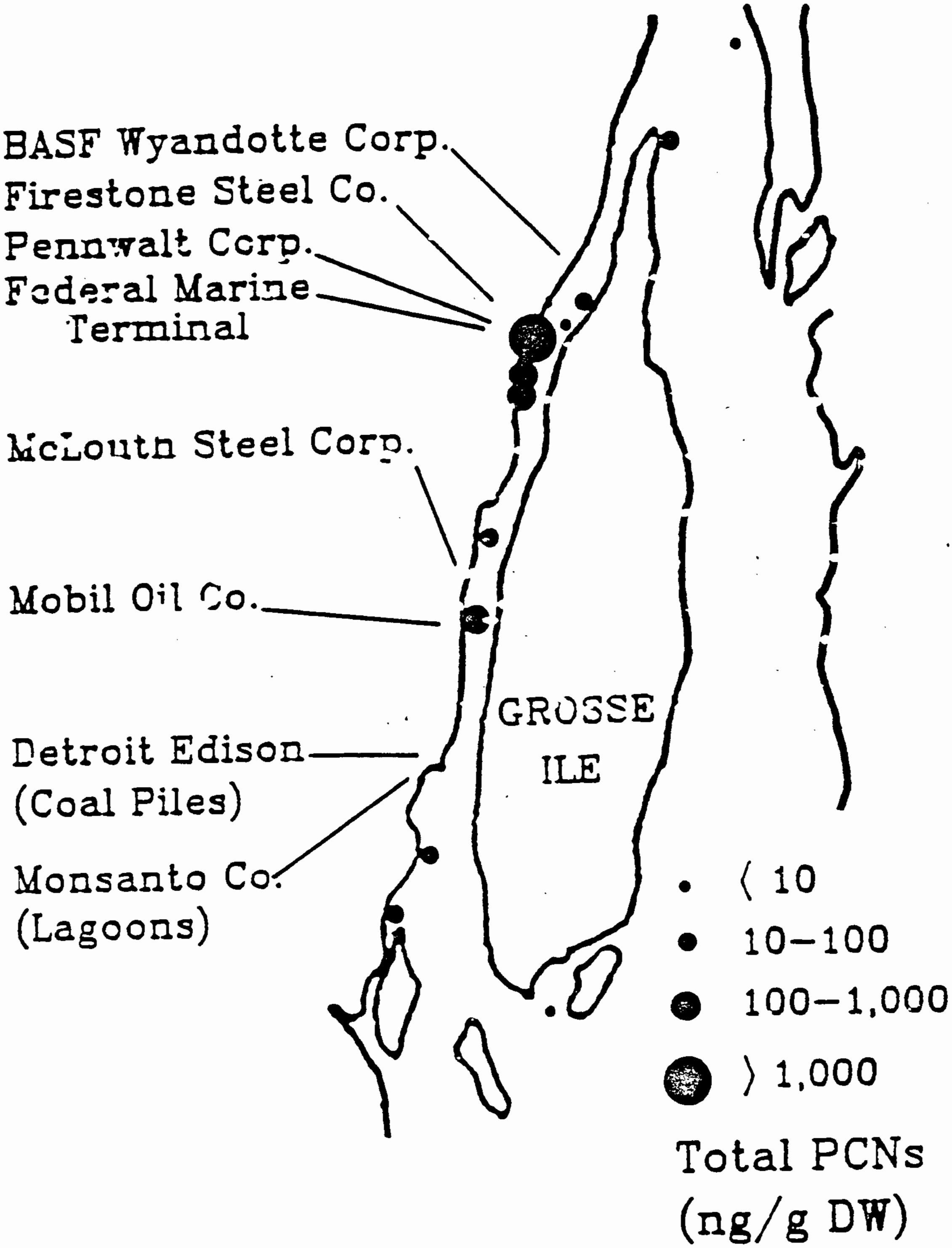


Figure 6 Trenton Channel sedimentary total polychlorinated naphthalene (PCN; sum of homologues) concentration distributions.

identified in Halowaxes examined in this study, suggesting sedimentary mixtures contain relatively greater abundances of higher Cl-homologues. The extent of commercial production of octachloronaphthalene is unknown.

Polychlorinated Terphenyls

Polychlorinated terphenyls (PCTs) are chlorinated terphenyl analogues of PCBs. Their production is a small fraction of PCBs (maximum U.S. PCT production: 20 x 10^6 lb. in 1971, Brinkman and de Kok, 1980), and they were commercially produced by Monsanto as pure PCT mixes (Aroclor 5400 series) and as PCB-PCT mixtures. PCTs are compositionally complex and are comprised of both chlorine positional isomers and positional isomers of the third phenyl ring (ortho, meta and para). As a result, gas and total ion chromatograms of both commercial PCT mixtures and sediment extracts are characterized by a poorly resolved mixture of broad peaks eluting at the end of a typical chromatogram (Figure 7). In this study, PCTs were quantified by summing the ion abundances of the most common PCT ions (corresponding to Cl-9 to Cl-14 homologues) and quantifying with respect to PCB congener 204, using a response factor determined for Aroclor 5460, a common PCT mixture. PCT concentrations are reported only as total PCT; no Cl homologue information has yet been generated. Total PCT distributions for the 12 sample subset are mapped in Figure 8 and listed in Table 4.

PCT concentrations range over 4 orders of magnitude, from a high of 15 ppm at Station 110 to undetectable concentrations both upstream and downstream of the Central Trenton Channel. Previous reports of environmental PCT contamination have associated particulate PCTs with investment casting facilities (Stratton and Sosebee, Jr., 1975). U.S. production of PCTs ceased in 1971, along with the cessation of PCB production. Increasing import of PCTs after 1971 were primarily for use in investment casting as a slow shrinkage wax

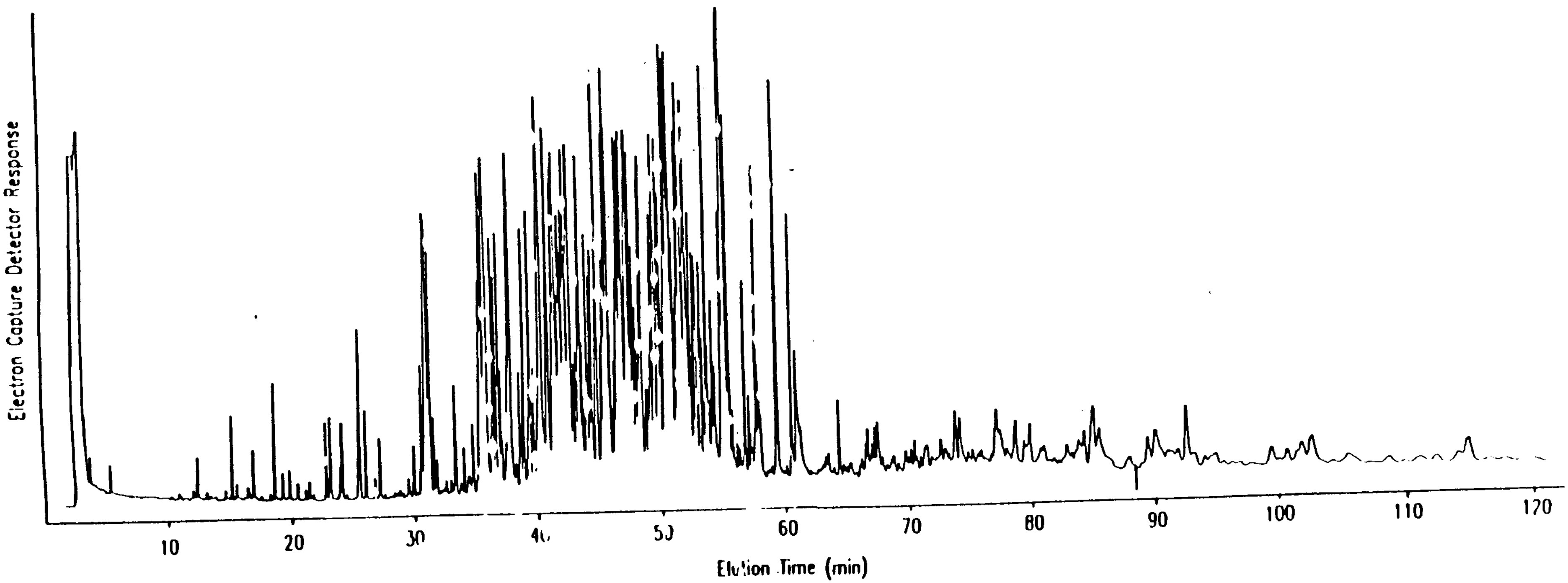


FIGURE 7 ELECTRON CAPTURE GAS CHROMATOGRAM OF STA. 110, 10% DICHLOROMETHANE FRACTION. CHROMATOGRAPHIC CONDITIONS IN TEXT.

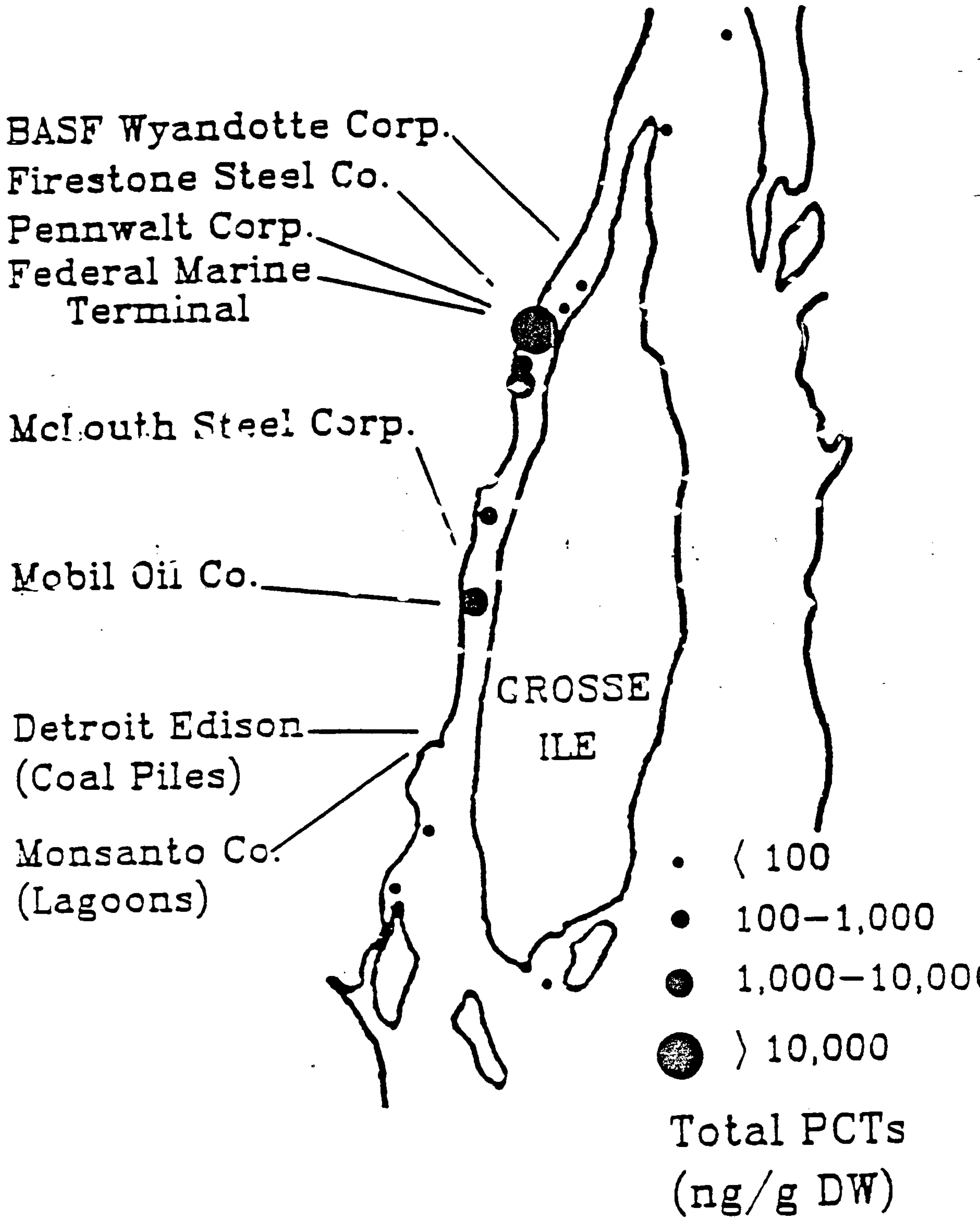


Figure 8 Trenton Channel sedimentary total polychlorinated terphenyl (PCT; see methods Appendix) concentration distributions.

filler (Brinkman and de Kok, 1980). This use, coupled with the absence of quantifiable PCTs at the beginning and end of Trenton Channel, suggest a localized Trenton Channel PCT source associated with one or several industrial concerns currently or formerly operating in the vicinity of Station 110. Station 110 is located adjacent to a closed steel products factory. However, other small, less well regulated commercial concerns are located in the region, as well as a significant hazardous waste site (the Federal Marine Terminal), so final linkage of PCTs to a source is tentative.

Polar Compounds: Surface sediment from station 30CR was analyzed in detail using gas chromatographic mass spectrometry (GC/MS) in methane enhanced electron capture negative ionization (ECNI) and electron impact (EI) ionization modes. Prior to analysis, the sample was separated into five fractions, the four most polar of which were examined. The three most polar fractions were methylated using CH_2N_2 in order to improve chromatography and determine if any compounds with acidic hydrogens were present in the sample. The purpose of these analyses was to characterize site 30CR through identification of the general compound classes and specific organic compounds present. Such characterization would help in determining if any unusual pollutants are likely to be found in the river. The major compound classes identified in sample 30CR include steroids, alkyl substituted naphthalenes, phthalates, carboxylic acids, and volatile halogenated species; based on this, it appears that possible contributors of organic contaminants to this site include sewage, nearby industry, and leachate from a landfill adjacent to the sampling site.

Sample 30CR is at the mouth of a small creek adjacent to the Federal Marine Terminal (FMT) in Riverview, Michigan. The FMT is a 30 acre patch of land jutting from the shore into the river. This land was used by BASF Wyandotte Corp. as a landfill for chemical/industrial materials from 1951 to

1979, at which time the dump site became the FMT. A 1979 study on the subsurface waters of the landfill indicated high levels of some organic compounds including naphthalenes, PAH's, and volatiles (J. Giesy, pers. commun). Station 30CR is also located near the Trenton sewage treatment plant and several industries, including a manufacturer of organic chemicals (Pennwalt Corp.). 30CR is one of the master stations in the IPPS, and it was found to be one of the most polluted with respect to PCB's, PCN's, PCT's, and PAH's (Furlong et al., 1987a). The sediment at this site also exhibits high toxicity in many bioassays such as Microtox, daphnid toxicity, and chironomid growth rate reduction (J. Giesy, pers. commun.). Both its chemical and toxicological properties, as well as its location (mid Trenton Channel), made this site worthy of detailed investigation. Observations and results presented in this report will allow for some insight into the likelihood of finding previously unidentified pollutants in the Detroit River system, and provide direction for the investigation of other sites.

Sediment from 30CR was Soxhlet extracted, and the extract was fractionated by absorption chromatography (silica gel) using C_6H_{14} - CH_2Cl_2 (9:1), CH_2Cl_2, CH_2Cl_2 - CH_3OH (98:2), CH_2Cl_2 -CH_3OH (92:8), and CH_3OH. All CH_3OH containing fractions were solvent exchanged into CH_2Cl_2 and divided into two subsamples each, one of which was subjected to derivatization while the other was unaltered. Derivatization was achieved by treating samples with 0.2M CH_2N_2 in hexane. All factions and subfractions were analyzed by ECNI (100' and 250'C) and EI GC/MS. GC temperature programming covered the range from 40'C to 280'C (4'/min., 94 min. total run time); masses from 50 to 750 amu were screened using the acquire mode. As is often the case when developing a new methodology, many procedures had to be modified and repeated. All analyses of the least polar fraction (C_6H_{14} - CH_2Cl_2) were disregarded because of its unexplainable chromatographic behavior (stripping of stationary phase); thus the results presented in this section do not include compounds which would be present in this fraction such as hydrocarbons, PCN's, PCB's, and PCT's.

Results of the analysis of 30CR are presented in Table 5. Carboxylic acids, phthalates, PAH's, and cholesterol related compounds were the most abundant classes identified; this implies that the sediment of 30CR is receiving an influx of sewage related materials and common industrial by-products. The presence of these compounds is not surprising given that both a waste water treatment plant and heavy industry are in the immediate vicinity. Alkyl substituted naphthalenes and some volatile organics were also found at this site. The FMT is a probable source of these compounds as they were found in high concentrations during a 1979 study of the landfill (J. Giesy, pers. commun.). The possible sources mentioned above are difficult to confirm at this stage given the ubiquity of the pollutants in question. Brominated phenols were among the more interesting compounds identified. Their source is unknown at present, but possible candidates include the FMT or industry upstream of 30CR. Although few truly novel pollutants were found, the investigation of site 30CR should prove useful in the continuing search for previously unknown pollutants in the Detroit River; the methods developed can be applied to the analysis of other sample sites, and results from 30CR will provide a guideline on what types of compounds can be expected.

The relationship between steroids and sewage is being studied to further understand the implications of the results obtained for 30CR. Also, the results of IPPS bioassays are being studied in relation to sewage and organic contaminant levels. Detailed investigation of polar fractions isolated from Detroit River sediments, using the methods outlined above, is continuing with the analysis of site 25 (north Grosse Ile) and site 105 (south Grosse Ile). sediments from both of these sites exhibit high toxicity. Additionally,

TABLE 5

Organic Compounds Identified in
Detroit River Sediment Sample 30CR

ALIPHATICS

Compound	Sample[1]	MS Method[2]	Retention(min.)	Relative Abundance
tetrachloroethene	CH_2Cl_2	100'	4.87	0
cyclohexenol	CH_3OH U	EI	9.152	+
cyclohexenone	CH_3OH U	EI	11.033	+
bicyclo(2,2,1)heptane	2% D	EI	5.839	+
2,4-octanedione	2% D	EI	21.243	+
myristic acid	8% U	EI	38.743	++
palmitic acid	8% U	EI	44.072	++++
stearic acid	8% U	EI	48.661	++++
dioctyl adipate	8% U	EI	52.827	++++
aliphatic ketones	2%, 8%, CH_3OH	EI	--	--
aliphatic amines	2%, 8%, CH_3OH	EI	--	--
aliphatic amides	2%, 8%, CH_3OH	EI	--	--
aliphatic alcohols	2%, 8%, CH_3OH	EI	--	--

SUBSTITUTED BENZENES

Compound	Sample[1]	MS Method[2]	Retention(min.)	Relative Abundance
dinitrophenol	2% U	100'	20.95	0
dibromophenol	CH_3OH U	100'	22.80	0
pentachlorobenzene	CH_2Cl_2	100'	28.20	0
hexachlorobenzene	CH_2Cl_2	100'	36.18	0
pentachloroaniline	CH_2Cl_2	100'	39.90	0
benzaldehyde	2% U	EI	10.593	+
thioanisole	CH_3OH D	100'	13.28	+
nitroaniline	8% U	100'	14.62	+
cresol	8% D	EI	17.491	+
dimethylphenol	CH_3OH U	EI	20.390	+
pentachloroanisole	CH_2Cl_2	100'	36.50	+
5-bromo-2-hydroxy-benzene ethanol	CH_3OH U	100'	38.98	+
pentachloro thio-anisole	CH_2Cl_2	100'	42.47	+
nitrophenols (2)	8% U	100'	15-19	++
benzoic acid	8% U	EI	19.879	++
dibromomethylphenol	CH_3OH U	100'	27.20	++
nonylphenols (4)	2% D	EI	39-41	++
dichlorobenzophenone	2% U	100'	41.08	++

SUBSTITUTED NAPHTHALENES AND BIPHENYLS

naphthaldehyde	2% U	100'	27.83	+
biphenyl	CH_2Cl_2	EI	28.968	+
isopropylnaphthalene	CH_2Cl_2	EI	33.170	+
methylnaphthalenes (2)	CH_2Cl_2	EI	26-27	++
dimethylnaphthalenes (4)	CH_2Cl_2	EI	29-31	++
trimethylnaphthalenes (5)	CH_2Cl_2	EI	34-36	++
methyl isopropylnaphthalenes (3)	CH_2Cl_2	EI	37-39	++
PCB's (Cl 4-10)	CH_2Cl_2	100'	--	--

PHTHALATES AND MISC.

phthalic acid	CH_3OH U	EI	26.658	+
alpha chlordane	CH_2Cl_2	100'	46.07	+
gamma chlordane	CH_2Cl_2	100'	46.80	+
nonachlors (2)	CH_2Cl_2	100'	47-50	+
butylbenzyl phthalate	8% U	100'	49.03	++
dioctyl phthalate	2% U	100'	52.55	+++
dibutyl phthalate	2% U	EI	55.142	+++
di(2-ethylhexyl)-phthalate	2% U	EI	57.071	++++

PAH's

acenaphthylene	CH_2Cl_2	EI	31.344	+
flourene	CH_2Cl_2	EI	35.650	+
coronene	CH_2Cl_2	100'	77.70	+
acenaphthene	CH_2Cl_2	EI	32.533	++
benzo(e)pyrene	CH_2Cl_2	100'	59.43	++++
benzo(a)pyrene	CH_2Cl_2	100'	61.78	++++
benzo(ghi)pyrelene	CH_2Cl_2	100'	66.05	++++

STEROIDS

cholestenone	8% U	EI	70.751	++
trimethylcholestanol	8% U	EI	73.417	++
cholestenes (2)	CH_3OH U	EI	63-64	+++
cholestadiene	CH_3OH U	EI	65.898	+++
cholestanone	8% U	EI	68.604	+++
methylcholestanol	8% U	EI	69.051	+++
dimethylcholestanols (2)	8% U	EI	72-73	+++
dimethylcholestenols (2)	8% U	EI	73-74	+++
cholestanols (2)	8% U	EI	67-68	++++
cholestenol	8% U	EI	67.458	++++

1 sample fractions, designated by eluting solvent from column chromatography:
CH_2Cl_2 - dichloromethane
2% - 2% methanol in dichloromethane
8% - 8% methanol in dichloromethane
CH_3OH - methane
D - derivatized with diazomethane
U - underivatized with diazomethane

2 100' - electron capture negative ionization
EI - electron impact

arrangements for the collection of sediment grab samples outside the Trenton Channel area are being made. Analysis of these samples will permit characterization of the entire river system and assessment of its potential for acting as a source of traceable compounds which could be used to study the fates of lipophilic organic pollutants introduced to the western basins of Lake Erie.

Comparisons of Polycyclic Aromatic Hydrocarbon Concentrations With Haloaromatic Compounds and Results From Other Investigators: PAH are significantly positively correlated with PCBs, PCNs, and PCTs concentrations (Table 6) determined thus far. PAH concentrations are also positively correlated with all the anthropogenic trace metals measured by the DePinto group (Cu, Ni, Zn, Pb, and Co) except for Cd and Cr. A plot of total Pb versus total PAH in Trenton Channel Sediments is shown in Figure 9. The lack of correlation for Cd and Cr may be due to remobilization in depositional environments that become anoxic, releasing Cd and Cr via pore water diffusion and subsequent downstream transport (M. Hermanson, pers. commun.).

PAH are significantly negatively correlated with several of the the toxicological parameters measured by the Giesy group. PAH concentration increases are correlated decreases in Chironomid growth rates and with decreased Daphnia LD_{10}s and LD_{50}s estimated for porewaters from Trenton Channel sediments. Total chironomid growth observations (in porewater) versus total sedimentary PAH concentrations are plotted in Figure 10. The small inset figure is the same plot less the data for Station 110, which has the highest PAH concentrations, but is not extremely toxic. Correlation with Microtox is not as satisfactory, and I suspect the reason is twofold: 1) Microtox are more sensitive to metal contamination than organic contaminants (J. Giesy, pers. commun.) and, 2) Microtox results for the Trenton Channel

Table 6. Correlation Matrix of Organic Contaminant Total Concentrations for Trenton Channel Sediments.

	Total PCNs	Total PCBs	Total PCTs	Total PAH
Total PCNs	1.00000			
Total PCBs	0.51786	1.00000		
Total PCTs	0.98099	0.58904	1.00000	
Total PAH	0.88382	0.77597	0.89718	1.00000

Critical Value (1 tail, 0.05) = ±0.49932; n=12

Figure 9. Total Polycyclic Aromatic Hydrocarbon (PAH) concentrations (ug/g dry weight of sediment) versus Total Lead (ug/g dry weight of sediment) in Trenton Channel surface sediments.

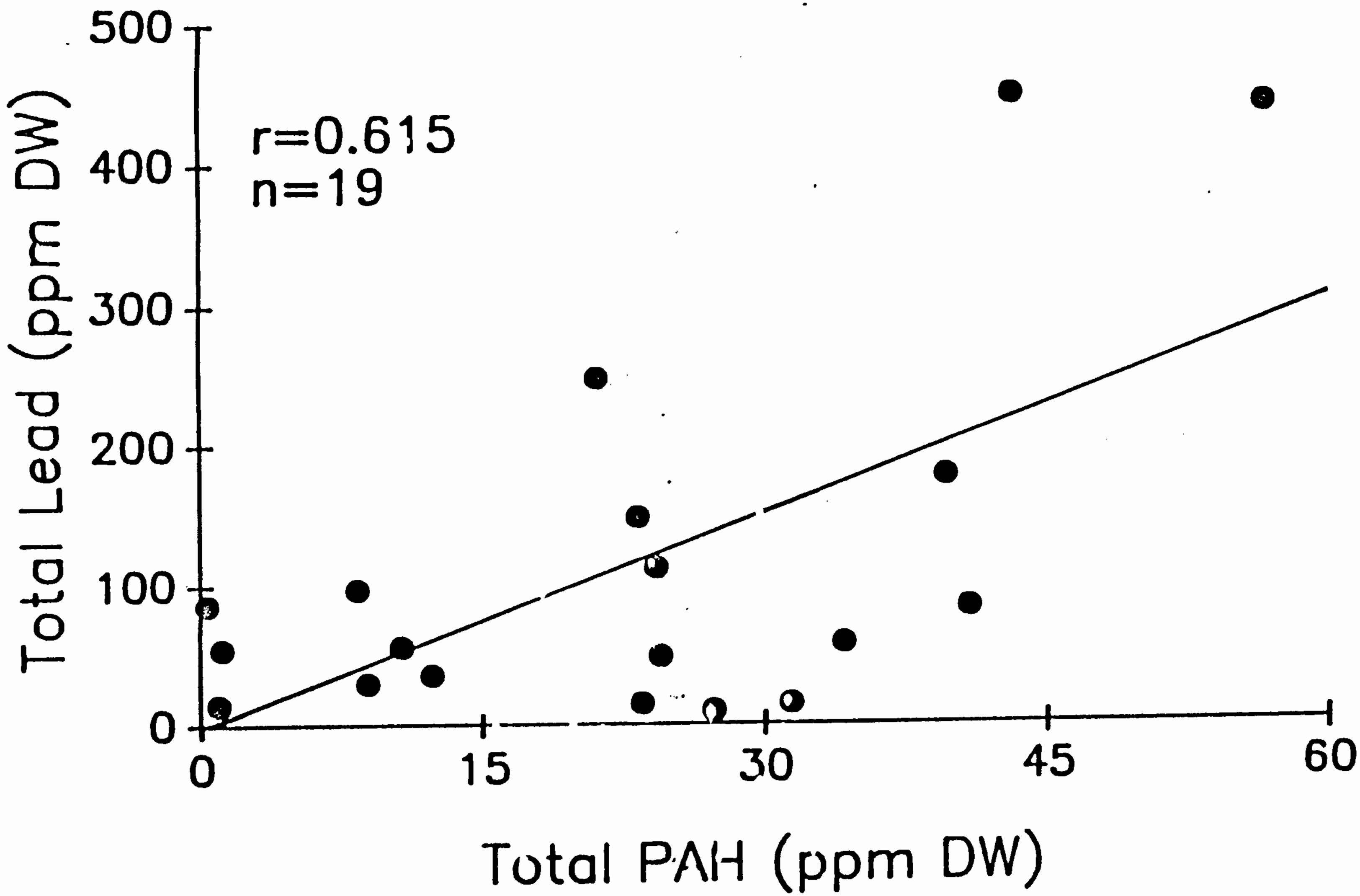
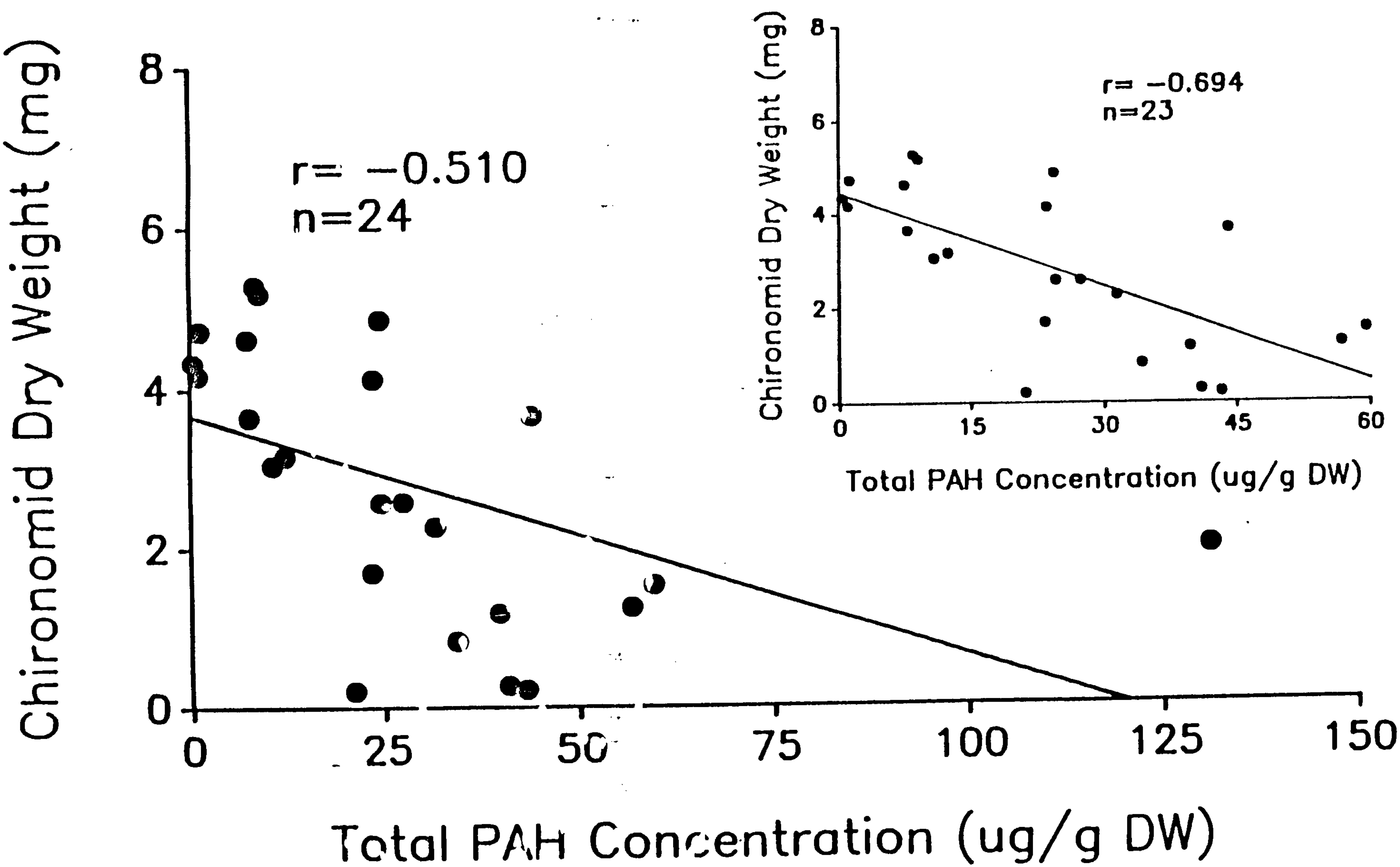


Figure 10. Chironomid Total Growth (as Dry Weight in mg) over ten days in porewaters from Trenton Channel sediments versus Total PAH concentrations (ug/g dry weight of sediment) in Trenton Channel sediments from the same stations. Inset graph is the same plot, less data from station 110.



cluster at both 0% and 100% toxicity, with few points in between.

Summary

Initial analyses of Trenton Channel sediments, with multiple trace organic analytical techniques, indicate a wide range of contaminant loading to sediments. Station 110, near Monguagon Creek, is the most contaminated site. All compound classes analyzed are most abundant at this site; there are low contaminant concentrations upstream of this station and decreasing contaminant concentrations downstream.

Determination of contaminant sources is complicated by multiple possible sources, both upstream of the channel and within the channel. Selective deposition of contaminant rich, fine-grained sediment within the channel results in increased heterogeneity of sample concentrations, further obscuring source-sink relationships.

In addition to the commonly measured PCBs and PAH, two novel classes of haloaromatic compounds, the polychlorinated naphthalenes (PCNs) and the polychlorinated terphenyls (PCTs) were identified and quantified. PCN and PCT distributions may emanate solely from a within-channel source and could serve as a unique chemical indicator of sediment transported organic contaminants from the Trenton Channel to Lake Erie.

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